

# Hierarchical dielectric orders in layered ferroelectrics $\text{Bi}_2\text{SiO}_5$

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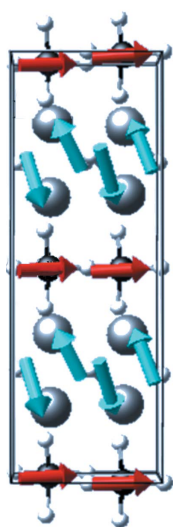
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Electric dipole engineering is now an emerging technology for high electron-mobility transistors, ferroelectric random access memory and multiferroic devices *etc.* Although various studies to provide insight into dipole moment behaviour, such as phase transition, order and disorder states, have been reported, macroscopic spontaneous polarization has been mainly discussed so far. Here, visualization of the electric dipole arrangement in layered ferroelectrics  $\text{Bi}_2\text{SiO}_5$  by means of combined analysis of maximum entropy charge density and electrostatic potential distribution analysis based on synchrotron radiation X-ray powder diffraction data is reported. It was found that the hierarchical dipole orders, the weak-ferroelectric and ferroelectric configurations, were observed in the  $\text{Bi}_2\text{O}_2$  and the  $\text{SiO}_3$  layers, respectively, and the ferroelectric configuration was realised by the interlayer interaction. This discovery provides a new method to visualize the local polarization in ferroelectric materials.

## 1. Introduction

Designing and controlling the intense local electric field and/or polarization in solids is vital for emerging electronics, such as high-performance field-effect transistors, ferroelectric random access memory and multiferroic devices in the nano-scale (de Araujo *et al.*, 1995; Auciello *et al.*, 1998; Haertling, 1999; Scott, 2000; Dawber *et al.*, 2005; Schilling *et al.*, 2007; Chung *et al.*, 2011; Yamada *et al.*, 2012; Keeney *et al.*, 2012a,b, 2013; Maity *et al.*, 2012; Zhang *et al.*, 2012). Dielectric properties have been mainly discussed in terms of macroscopic properties based on measurements of dielectric permittivity ( $\epsilon$ ) and electric polarization ( $P$ ) under electric fields ( $E$ ) for bulk samples so far. Recently, electrostatic potential (EP) analysis based on electron charge density (ECD) using the maximum entropy method (MEM) has been developed for the characterization of specific features originating from the electrostatic field/force on the microscopic scale (Sakata & Sato, 1990; Takata & Sakata, 1996; Takata, 2008; Tanaka *et al.*, 2006; Kim *et al.*, 2011). Using ECD/EP analysis, we succeeded in visualizing the relationship between internal electric fields and physical properties, such as thermal conductivity affected by rattling (Fujiwara *et al.*, 2012) and superconductivity related to the bi-polaron (Kim *et al.*, 2014).



$\text{Bi}_2\text{SiO}_5$  (BSO) has attracted much attention as an alternative to the traditional lead-based ferroelectric materials with a phase-transition temperature ( $T_c$ ) of 673 K. BSO has an Aurivillius-like structure consisting of the  $[\text{Bi}_2\text{O}_2]^{2+}$  layer and  $[\text{SiO}_3]^{2-}$  layer (Fig. 1a) (Pirovano *et al.*, 2001; Georges *et al.*, 2006; Taniguchi *et al.*, 2013). A relatively large spontaneous polarization ( $P_c$ ) of  $14.5 \mu\text{C cm}^{-2}$  along the  $\text{SiO}_3$  chain ( $c$ -axis) was predicted by first-principles calculations, while those along the  $a$ - and  $b$ -axes,  $P_a$  and  $P_b$ , are estimated to be small,  $0.1 \mu\text{C cm}^{-2}$  and  $0 \mu\text{C cm}^{-2}$ , respectively (Taniguchi *et al.*, 2013). From experimental  $P$  versus  $E$  measurements (Taniguchi *et al.*, 2013), only the  $P_a$  value of  $0.8 \mu\text{C cm}^{-2}$  was detected, because the BSO crystals have a thin-plate shape, and the electrode for the  $P$  versus  $E$  measurements can only be formed on a large area of the  $b$ - $c$  plane of the crystals. In addition, the polarization of BSO is suggested to originate from the  $\text{SiO}_3$  layer and not from the  $\text{Bi}_2\text{O}_2$  layer by the first-principles calculations (Taniguchi *et al.*, 2013). Clarification of the origin and mechanism of the ferroelectricity in BSO is therefore crucial for further development of lead-free ferroelectric materials.

Here, we report the visualization of the electric dipole arrangement in layered ferroelectrics  $\text{Bi}_2\text{SiO}_5$  by means of combined analysis of the ECD using MEM and EP distribution analysis based on high-precision synchrotron radiation X-ray powder diffraction data.

## 2. Experimental

Synchrotron radiation X-ray powder diffraction measurements of BSO were performed at BL02B2 beamline at SPring-8 with a large Debye–Scherrer camera to obtain high counting statistics for accurate structure analysis (Nishibori *et al.*, 2001; Takata *et al.*, 2002). The BSO sample was sufficiently ground

for a homogeneous distribution of intensity and sealed in a glass capillary with a diameter of 0.1 mm. The diffraction pattern was measured at 300 K and 773 K with a  $\text{N}_2$  gas flowing temperature control system. The measurement wavelength was  $0.35206(1) \text{ \AA}$  to reduce absorption effects caused by the heavy atom (Bi) in the sample. The diffraction data were collected for 45 min on an image plate installed in the large Debye–Scherrer camera.

Determination of the precise structure was carried out by Rietveld refinement. Details of the process and the results are described in the supporting information. The total number of observed structure factors was 3921 and 2930 at 300 K and 773 K, respectively. The ECD was calculated by MEM using the *ENIGMA* program (Sakata *et al.*, 1990; Tanaka *et al.*, 2002). The electrostatic potential was calculated with a method developed by Tanaka *et al.* using the MEM electron charge density (Tanaka *et al.*, 2006). The electrostatic potential  $[U(r)]$  is composed of the nucleus charge  $[U_{\text{nuc}}(r)]$  and the electron charge  $[U_{\text{ele}}(r)]$  components. In this study, ECD and EP were visualized using the *OpenDx* program provided by IBM Visualization Data Explorer. The procedure for the polarization calculations is described in the supporting information.

## 3. Results

The ECD/EP analysis is one of the best ways to understand the microscopic behaviour of polarizations in BSO. The ECD distributions directly obtained from integrated intensities of the X-ray diffraction pattern by MEM analysis reveal the deformation of both the  $\text{BiO}_4$  square pyramids in the  $\text{Bi}_2\text{O}_2$  layer and the  $\text{SiO}_3$  tetrahedra in the  $\text{SiO}_3$  layer [Figs. 1(b)–1(e)]. In the ferroelectric phase (300 K), the Bi atoms form a stronger covalent bond with one of the four equivalent first-

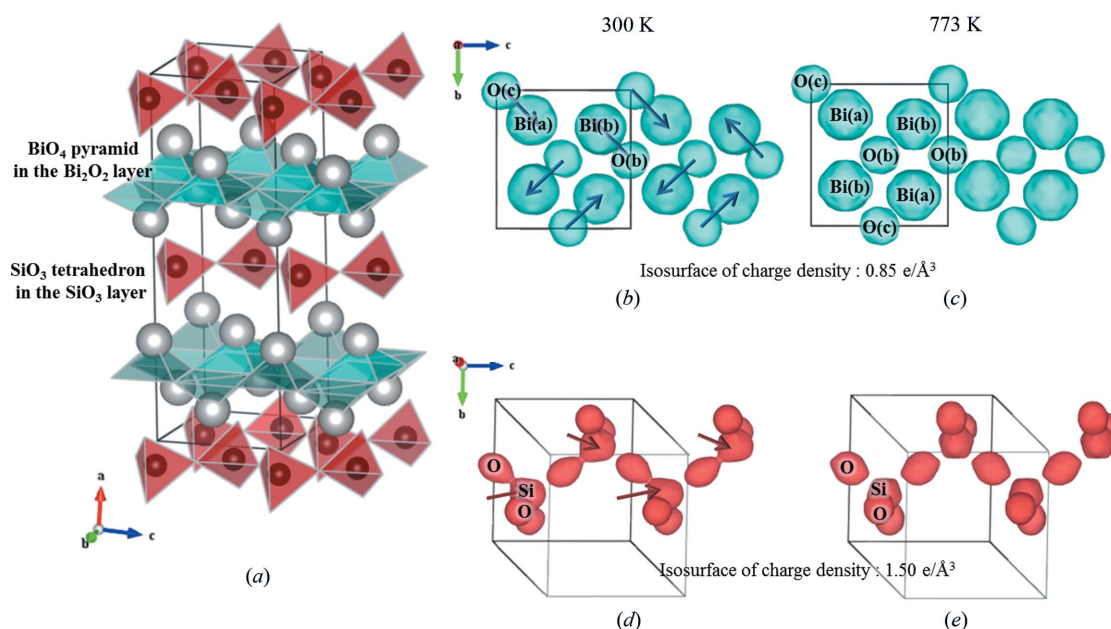


Figure 1

Schematic drawing of the crystal structure (a) and ECD using MEM distribution of the  $\text{Bi}_2\text{O}_2$  (b, c) and the  $\text{SiO}_3$  layer (d, e) in the ferroelectric (300 K) and paraelectric (773 K) phases. The isosurface of ECD is  $0.85 \text{ e \AA}^{-3}$  and  $1.50 \text{ e \AA}^{-3}$  for the  $\text{Bi}_2\text{O}_2$  and the  $\text{SiO}_3$  layer, respectively.

neighbour O atoms in the paraelectric phase (773 K) (see Fig. S4 and Table S4 of the supporting information). The Bi(*b*)-O(*b*) and Bi(*a*)-O(*c*) pairs form electric dipole moments, and the two neighbouring electric dipoles form an almost antiparallel configuration in the Bi<sub>2</sub>O<sub>2</sub> layer (Fig. 1*b*). On the other hand, the Si atoms in the ferroelectric phase form a stronger covalent bond (Fig. 1*d*) with three of the four equivalent first-neighbour O atoms in the paraelectric phase (Fig. 1*e*), showing that the SiO<sub>3</sub> cluster has an electric dipole moment. The electric dipoles of SiO<sub>3</sub> align in the ferroelectric configuration. From the ECD analysis using MEM, the results visualized the antiferroelectric order in the Bi<sub>2</sub>O<sub>2</sub> layer and the ferroelectric order in the SiO<sub>3</sub> layer in the ferroelectric phase, as shown in Figs. 2(*a*) and 2(*b*). This is the reason why the large dipole moment of BSO originates from the SiO<sub>3</sub> layer instead of the Bi<sub>2</sub>O<sub>2</sub> layer.

Electric dipole moments in the crystal can be calculated from the electron charge using MEM and the nuclear charge using Ewald's method. It is, however, well known that the value of the polarization calculated from the charge distribution strongly depends on the method of selection of the crystallographic unit cell: the determination of the boundary of the crystallographic unit cell is critical for the calculation (Resta & Vanderbilt, 2007; Spaldin, 2012). This issue can be resolved by the Berry-phase theory (King-Smith & Vanderbilt, 1993; Resta, 1994; Neaton *et al.*, 2005). In the current case, we introduce the concept of fragments for extracting experimentally individual dipole units originating from BiO and SiO<sub>3</sub> clusters. The boundary of fragments can be determined by the local minimum value of EP around the fragments

(ECD/EP method) so that each fragment satisfies charge neutrality. An extracted fragment unit of SiO<sub>3</sub> is shown in Fig. 3 as an example. The partial electric polarization in the fragments can be estimated by (Spaldin, 2012; Gohda *et al.*, 2000)

$$\mathbf{P} = \frac{e}{V} \left\{ \sum_i A_i [(X_i - x_o)\hat{x} + (Y_i - y_o)\hat{y} + (Z_i - z_o)\hat{z}] - \left[ \int (x_i - x_o)\rho_i(x_i) dx_i \hat{x} + \int (y_i - y_o)\rho_i(y_i) dy_i \hat{y} + \int (z_i - z_o)\rho_i(z_i) dz_i \hat{z} \right] \right\}, \quad (1)$$

where  $V$  is the volume of the unit cell;  $e$  is the elementary charge ( $1.602 \times 10^{-19}$  C);  $A_i$  is atomic number;  $(X_i, Y_i, Z_i)$  is the position of  $i$ th atom;  $(x_o, y_o, z_o)$  is the position of the center of mass in the fragment unit;  $\rho_i(x_i, y_i, z_i)$  is the electron density located at the  $i$ th pixel;  $(x_i, y_i, z_i)$  is the position of  $i$ th pixel for electron charge contribution;  $(\hat{x}, \hat{y}, \hat{z})$  is the unit vector. Integration is carried out over the fragment unit; the value of the electron density is assigned to pixels in a unit cell divided into  $256 \times 128 \times 128$  pixels. The total and projected values of polarization are summarized in Table 1.

The SiO<sub>3</sub> layer shows a large polarization along the *c*-axis originating from a large dipole moment of the SiO<sub>3</sub> fragment [ $27.3(1) \mu\text{C cm}^{-2}$ ]. The projected values of the polarization along the *a*- and *c*-axis,  $P_a$  and  $P_c$ , in the SiO<sub>3</sub> layer are  $1.4(1) \mu\text{C cm}^{-2}$  and  $27.3(1) \mu\text{C cm}^{-2}$ , respectively. It should be noted that  $P_b$  is zero due to the inversion symmetry operation along the *b*-axis. On the other hand, the Bi<sub>2</sub>O<sub>2</sub> layer has a small but distinct polarization value in spite of the

antiferroelectric order: the projections of the polarization in the Bi<sub>2</sub>O<sub>2</sub> layers were  $-1.8(1) \mu\text{C cm}^{-2}$  for  $P_a$  and  $-3.8(1) \mu\text{C cm}^{-2}$  for  $P_c$ . This originates from the asymmetric distortion of the Bi<sub>2</sub>O<sub>2</sub> pyramids, meaning that the Bi-O dipoles with antiparallel configuration do not fully cancel out the polarization in the layer: this is regarded as the weak-ferroelectric configuration, as shown in Fig. 2(*c*). Since the residual polarization in the Bi<sub>2</sub>O<sub>2</sub> layer aligns in the antiparallel direction to the polarization in the SiO<sub>3</sub> layer, the distortion in the Bi<sub>2</sub>O<sub>2</sub> layer is suggested to be induced by the large polarization of the SiO<sub>3</sub> layer for reducing the electrostatic energy in the crystal. The individual dipole moment [ $26.8(3) \mu\text{C cm}^{-2}$  and  $27.0(4) \mu\text{C cm}^{-2}$ ] of Bi-O is comparably large with that of the SiO<sub>3</sub> fragment [ $27.3(1) \mu\text{C cm}^{-2}$ ], although the net value is as small as  $4.2(1) \mu\text{C cm}^{-2}$  owing to the antiparallel configuration of the Bi-O dipoles.

The total  $P_a$  and  $P_c$  of BSO were estimated to be  $0.3(2) \mu\text{C cm}^{-2}$  and

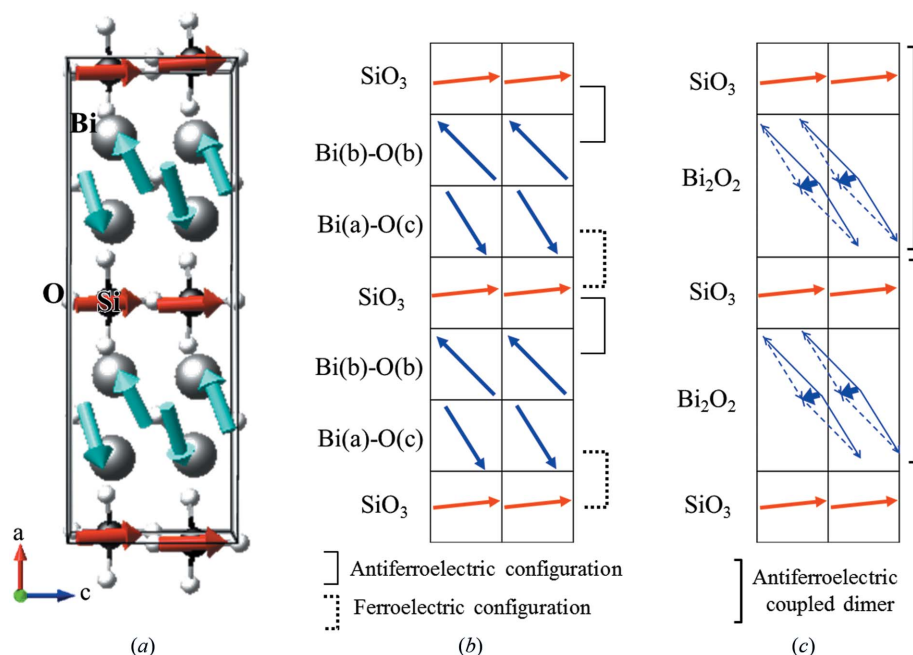


Figure 2

Schematic of the electric dipole configuration of Bi<sub>2</sub>SiO<sub>5</sub> based on the polarization obtained by the ECD/EP method. (*a*) Three-dimensional electric dipole configuration with atom positions. (*b*) Schematics of dipole ordering for SiO<sub>3</sub>, Bi(*b*)-O(*b*) and Bi(*a*)-O(*c*). (*c*) Schematic dipole ordering showing a weak-ferroelectric configuration of the Bi<sub>2</sub>O<sub>2</sub> layer. The residual dipole in the Bi<sub>2</sub>O<sub>2</sub> layer is aligned antiparallel to the large dipole in the SiO<sub>3</sub> layer showing the ferroelectric configuration.

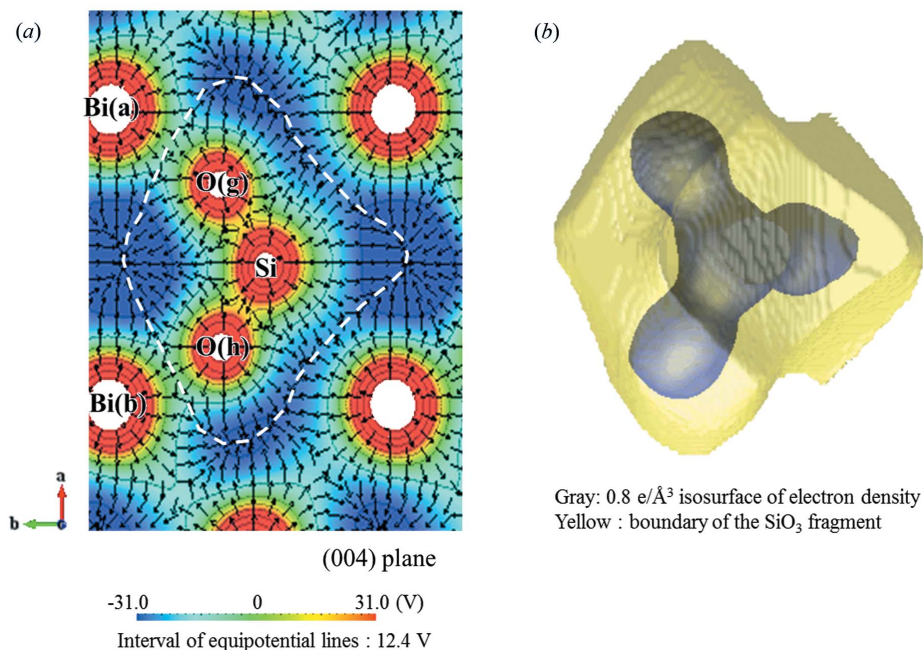


**Figure 3**  
Extracted SiO<sub>3</sub> fragment. (a) Two-dimensional EP map on the (004) plane with electric fields. The boundary defining the dipole unit can be determined by the local minimum value of the EP around the fragments (white dashed line). (b) Extracted three-dimensional perspective of the SiO<sub>3</sub> fragment area (yellow) with the shape of the SiO<sub>3</sub> molecule with an isosurface of 0.8 e Å<sup>3</sup> (grey).

23.5 (1)  $\mu\text{C cm}^{-2}$ , respectively.  $P_b$  was zero because of the symmetry operation of the crystal structure. The value of  $P_a$  is roughly consistent with that predicted by theoretical calculation (0.1  $\mu\text{C cm}^{-2}$ ) and that determined by  $P$  versus  $E$  measurements (0.8  $\mu\text{C cm}^{-2}$ ) (Taniguchi *et al.*, 2013). In addition, the large  $P_c$  value predicted by theoretical calculation [14.5  $\mu\text{C cm}^{-2}$ ] was experimentally determined by a microscopic approach using ECD/EP analysis [23.5 (1)  $\mu\text{C cm}^{-2}$ ]. The result shows that the ECD/EP analysis using precise X-ray diffraction data can derive the local electric dipole moment in the crystal as well as in the polarization values from small amounts (less than 0.1 mg) of powder samples, and values are consistent with those

predicted by the complete picture based on the Berry-phase theory. It should be noted that the values of polarization based on the point charge model, where the electron charge of atoms was assigned to each atomic position obtained by Rietveld analysis, largely deviated from any other results of theoretical prediction,  $P$  versus  $E$  measurements and the ECD/EP analysis; this result shows that the use of the ECD distribution is essential for estimation of accurate values of polarization. The method of ECD/EP analysis is, therefore, useful for characterization and design of newly synthesized dielectric materials, and thus for the development of emerging dielectric materials.

The hierarchical dipole ordering with structural distortion can be understood in terms of electrostatic energy. Firstly, the antiferroelectric configuration with the residual dipole moments (weak ferroelectricity) and the ferroelectric configuration are realised in the Bi<sub>2</sub>O<sub>2</sub> and the SiO<sub>3</sub> layer, respectively. Next, the antiparallel arrangement between the net small dipoles in the Bi<sub>2</sub>O<sub>2</sub> layer and the large dipoles in the SiO<sub>3</sub> layers reduces the interlayer electrostatic interaction; this configuration is regarded as an interlayer ferrielectric ordering. In addition, the neighbouring Bi<sub>2</sub>O<sub>2</sub> and SiO<sub>3</sub> layers form a pair, namely, the dimerization of the layers (Figs. 2c and S3a). In this distortion the dipoles in the neighbouring layer being aligned in the antiparallel configuration become close to reduce the electrostatic energy. In actual fact, the cohesive energy of the low-temperature ‘ferroelectric’ phase is lower than that of the high-temperature paraelectric phase by 23.1 meV in Bi<sub>2</sub>SiO<sub>5</sub> (Taniguchi *et al.*, 2013), showing an energetic advantage of the ‘ferroelectric’ phase with hierarchical dipole ordering.

The ECD/EP analysis can visualize the properties of covalency and polarization in the crystal using a tiny amount of powder sample. In addition, the method demonstrates its ability to visualize local polarization which cannot be detected by the macroscopic measurements in principle. In the case of BSO, for instance, a large dipole moment should be induced at the SiO<sub>3</sub> layer, and large polarization is stabilized by the antiparallel configuration with the Bi<sub>2</sub>O<sub>2</sub> layer.

**Table 1**  
Total and projected polarization estimated by the ECD/EP method, point charge model (PC model),  $P$  versus  $E$  measurement and first-principles calculation.

$P$  versus  $E$  measurements and the first-principles calculation are reported by Taniguchi *et al.* (2013). All values are shown in units of  $\mu\text{C cm}^{-2}$ .

|                              |                                                            | Total polarization | Projected polarization |       |           |
|------------------------------|------------------------------------------------------------|--------------------|------------------------|-------|-----------|
|                              |                                                            | $ P $              | $P_a$                  | $P_b$ | $P_c$     |
| ECD/EP method                | Bi <sub>2</sub> O <sub>2</sub> layer                       | 4.2 (1)            | −1.8 (1)               | 0     | −3.8 (1)  |
|                              | Bi(b)–O(b) sublayer<br>(upper square-pyramid<br>component) | 26.8 (3)           | 24.0 (3)               | 0     | −11.9 (1) |
|                              | Bi(a)–O(c) sublayer<br>(lower square-pyramid<br>component) | 27.0 (4)           | −25.8 (4)              | 0     | 8.0 (1)   |
|                              | SiO <sub>3</sub> layer                                     | 27.3 (1)           | 1.4 (1)                | 0     | 27.3 (1)  |
|                              | Bi <sub>2</sub> SiO <sub>5</sub>                           | 23.5 (1)           | 0.3 (2)                | 0     | 23.5 (1)  |
| PC model                     | Bi <sub>2</sub> SiO <sub>5</sub>                           | 9.4                | 4.9                    | 0     | 8.1       |
| $P$ versus $E$ measurement   | Bi <sub>2</sub> SiO <sub>5</sub>                           | –                  | 0.8                    | –     | –         |
| First-principles calculation | Bi <sub>2</sub> SiO <sub>5</sub>                           | 14.5               | 0.1                    | 0     | 14.5      |

#### 4. Summary

In summary, we have discovered a new approach to the visualization of the local electric dipole moments and their orders in a crystal by means of the combined analysis of ECD using MEM and EP distribution analysis based on synchrotron radiation X-ray powder diffraction data. Application of this method revealed hierarchical dipole ordering in  $\text{Bi}_2\text{SiO}_5$ : the weak ferroelectricity in the  $\text{Bi}_2\text{O}_2$  layer, the ferroelectric order in the  $\text{SiO}_3$  layer, and the ferroelectric order between the  $\text{Bi}_2\text{O}_2$  and  $\text{SiO}_3$  layers. The results suggest that ECD/EP analysis is a useful method to visualize the local polarization based on X-ray powder diffraction experiment.

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